QUARTERLY TECHNICAL REPORT
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We report the results of our research activities under NREL Subcontract ADJ-2-30630-17 during the third quarter of Phase III. During this quarter we have been working on two projects primarily related to the Narrow Gap Materials reporting umbrella: Examining the properties of nanocrystalline samples (nc-Si:H) obtained from United Solar Ovonics Corporation, and the properties of HW a-Si,Ge:H alloys produced at NREL.

First of all, we will discuss the most recent results of our continuing experimental work to characterize the nc-Si:H samples from USOC. These most recent measurements have been carried out on Sample 14657 which consists of 3-layer sandwich --700nm thick nc-Si:H layer clad between two 200 to 250nm thick a-Si:H layers in a SS/n+/a-Si:H/nc-Si:H/a-Si:H/Pd structure. As we reported previously, transient photocapacitance (TPC) spectra on the USOC nc-Si:H samples exhibit a marked temperature variation such that, at the lowest temperatures, they are nearly identical to spectra for microcrystalline Si obtained elsewhere using the CPM method while, at higher temperatures, the TPC spectra appear much more similar to sub-band-gap spectra normally obtained for amorphous Si (a-Si:H). A recent set of such spectra for sample 14657 taken over a wide range of measurement temperatures is shown in Fig. 1.

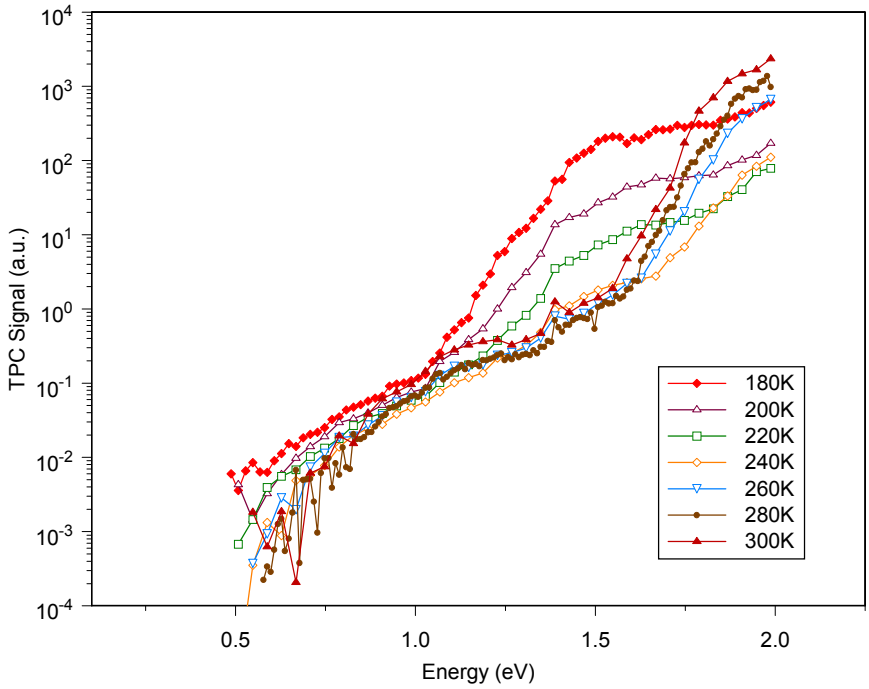

FIG. 1. Transient photocapacitance spectra for sample 14657 obtained over a wide range of measurement temperatures. Measurements were carried out at 80kHz under a –3V ambient bias with voltage filling pulses to 0V.

As we have discussed previously, the variation in the appearance of the photocapacitance spectra indicates the mixed phase nature of the United Solar nc-Si:H material. Specifically, we believe that the progression of these spectra from being more μc-Si:H like at lower temperatures to more a-Si:H like at higher temperatures is due to the suppression of the crystallite signal component when *more of the minority carriers are able to escape* the depletion region during the TPC measurement time window. This cancels the charge change (and hence the photocapacitance signal) caused by the escape of the optically excited majority carriers that dominates the appearance of the spectra at the lower temperatures. In contrast, the minority carriers generated in the amorphous silicon component of the sample appear to remain trapped and so this component of the sample dominates the spectra above 280K.

This means, in particular, that the *higher* the magnitude of the TPC signal near 1.5eV (where the microcrystalline Si absorption tends to dominate) the lower the hole collection fraction will be for carriers generated in the microcrystalline component of this nc-Si:H sample. In our previous Quarterly, we reported that prolonged light exposure also reduces the fraction of holes collected. In Fig. 2 we display two sets of spectra for sample 14657. In Fig. 2(a) we show the effect of reducing the temperature from 240K to 180K. We observe that the TPC signal near 1.5eV increases by more than a factor of 30, indicating that the hole collection fraction has been substantially reduced at 180K compared to 240K. In Fig. 2(b) we display the effect on the 240K TPC spectrum of light soaking for 100 hours to 610nm filtered ELH light at an intensity of 100mW/cm^2. The resulting spectrum is quite similar to that obtained by lowering the measurement temperature, indicating a similar decrease in hole collection.

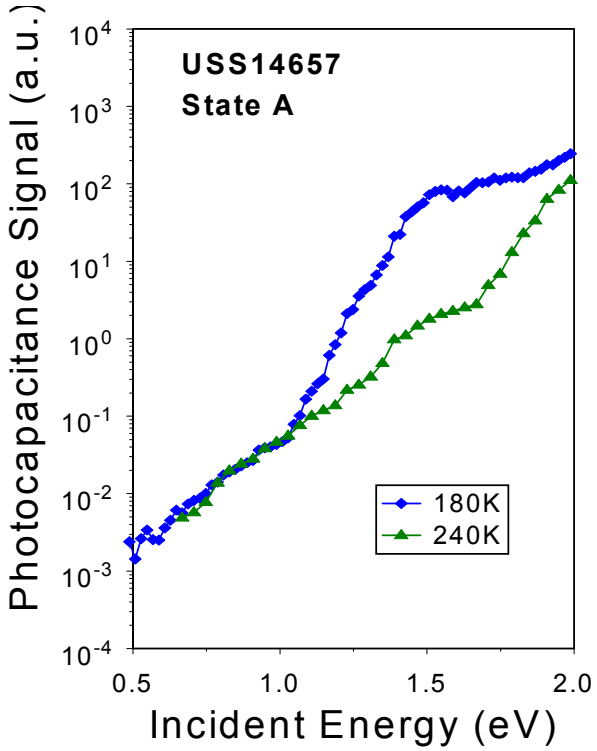

FIG. 2(a). Photocapacitance spectra in State A at two temperatures showing the decrease in hole collection as the temperature is lowered.

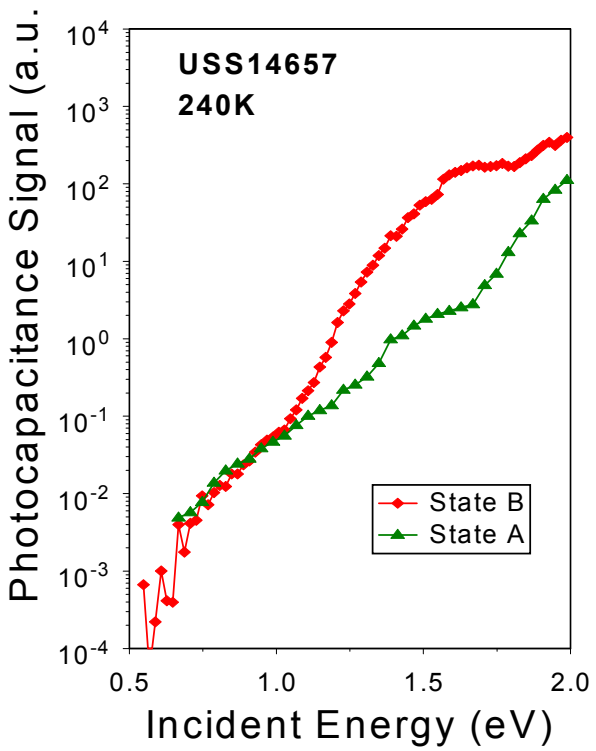

FIG. 2(b). Comparison of annealed and light-degraded photocapacitance spectra at 240K. This clearly shows that prolonged light exposure reduces the hole collection.

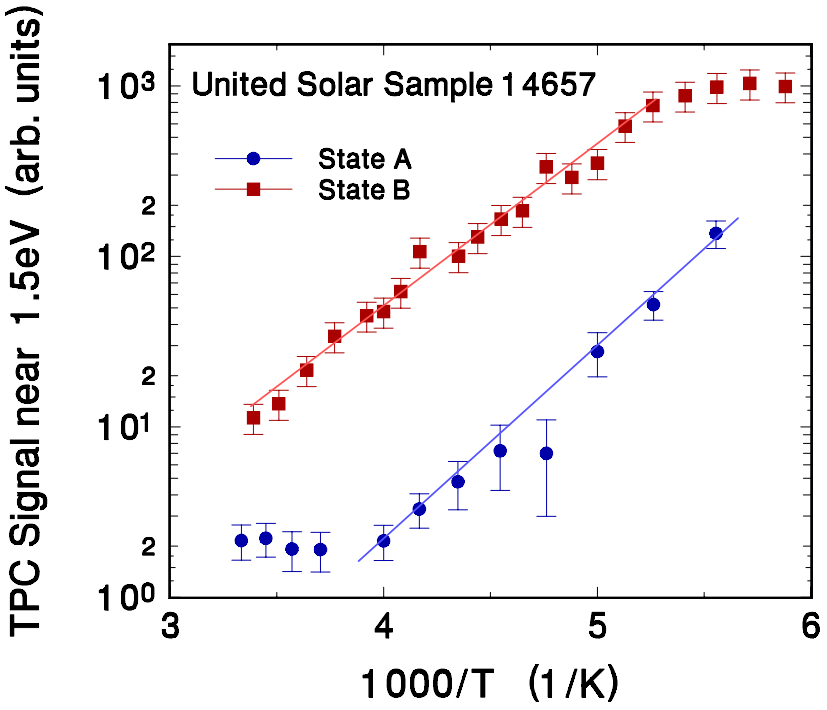

FIG. 3. Arrhenius plot showing the temperature dependence of the TPC signal near 1.5eV for both the annealed and light-degraded states of nc-Si:H sample 14657. The *lower* the TPC signal, the *higher* the hole collection fraction. In both cases the temperature dependence appears to be thermally activated, with similar activation energies (near 0.2eV), but with relative values that differ by more than a factor of 30.

In spite of the clear reduction in hole collection, Fig. 2(b) indicates that the light exposure does *not* appear to increase the deep defect density (dangling bonds). Thus, the root cause of the decrease in hole collection is not yet understood.

To try to gain some additional insight into the cause of the reduced hole collection, we have determined the magnitude of the TPC signal as a function of temperature near 1.5eV in more detail. This is plotted in Fig. 3 in Arrhenius form for both the annealed (State A) and light degraded state (State B) of this sample. As we see, for both cases the hole collection fraction vs. temperature appears to be thermally activated, with characteristic energies near 0.2eV in both cases. This may therefore suggest a predominant hole trap near the valence band edge which increases in magnitude after prolonged light exposure. This trap does not appear to be simply related to the dangling bond defects in the a-Si:H component of the sample, although it could still originate from the a-Si:H component of these mixed phase samples, or from the boundary region between the two phases. This suggests the potential value of future experiments which compare the degree of light induced effects for nc-Si:H samples which contain varying fractions of the a-Si:H component.

Our second focus during this quarter has been on a-Si,Ge:H alloys produced by the HWCVD process. A series of seven samples with Ge fractions of 0, 15, 29, 47, 63, 81, and 100at.% were obtained from Yueqin Xu and Harv Mahan at NREL. These 1.2 to 1.6 micron thick alloy films were deposited onto n^+ a-Si:H coated stainless steel at substrate temperatures that varied during deposition – typically between 200°C at the beginning to an average of 290°C at the end. Tauc gaps ranged between 1.65eV for the 15at.% alloy sample to 0.98eV for the a-Ge:H endpoint film. More details are given in Table I. These films were deposited using a Ta filament that was operated a lower temperature (≤1800°C) than the NREL HWCVD a-Si,Ge:H samples we have studied in the past (those were deposited with a tungsten filament wire at temperatures of at least 2000°C).

TABLE I. Characteristics of HWCVD a-Si,Ge:H films obtained from NREL. All samples were deposited on n^+ a-Si:H coated Stainless Steel substrates. The substrate temperature at the beginning of each a-Si,Ge:H layer deposition was 200°C.

Sample	Thickness (μm)	Ge fraction (at.%)	T_{sub} at end (°C)	Dep. Rate (Å/s)	E_{04} (eV)	E_{Tauc} (eV)
L1304	1.75	0	309	1.62	1.90	1.74
L1305	1.50	15	295	1.39	1.79	1.65
L1306	1.60	29	293	1.78	1.66	1.50
L1307	1.44	47	292	2.00	1.47	1.32
L1308	1.38	63	286	2.56	1.40	1.22
L1309	1.15	81	275	3.14	1.28	1.12
L1310	1.18	100	279	3.27	1.05	0.98

During the past Quarter we only had time to characterized one sample in any detail: the 29at.% Ge (L1306) device. For this sample we carried out admittance measurements, drive-level capacitance profiling, and TPC spectroscopy. Only the fully annealed state of this sample has been examined so far.

Drive-level profiles for this sample are displayed in Fig. 4. These indicate a surprisingly low deep defect density for such an a-Si,Ge:H alloy: below 7×10^{15} cm^{-3} over a substantial fraction of this film. This is comparable to the best PECVD a-Si,Ge:H samples in this composition range. There is, however, considerable more spatial variation than is usually observed for the PECVD alloy samples, most likely due to the substantial drift in substrate temperature during growth.

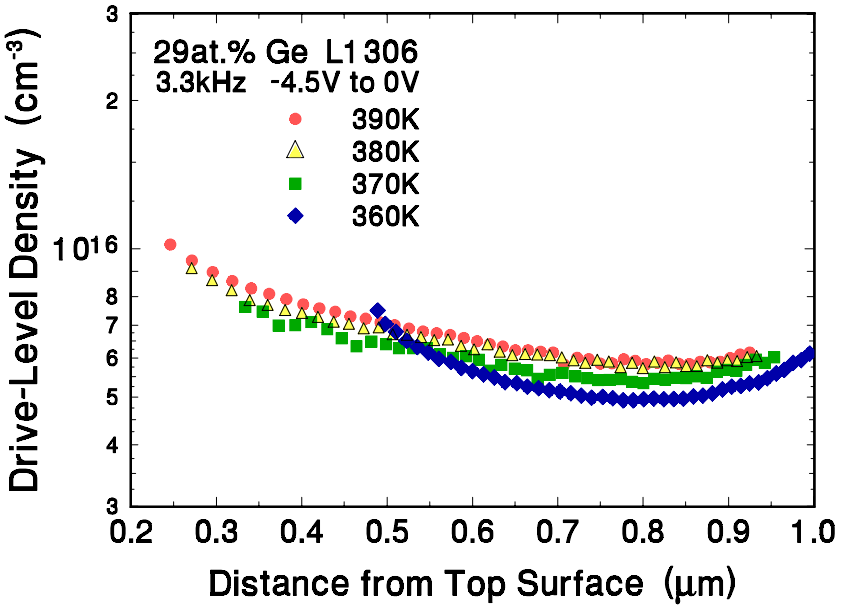

FIG. 4. DLC profiles for the 29at.% HWCVD alloy film. The profiles reach a clear limiting value at 390K, and this indicates the deep defect density in this sample. The larger spatial variation exhibited by the 360K profile is an artifact due to the partial onset of dielectric freeze-out at this temperature and frequency.

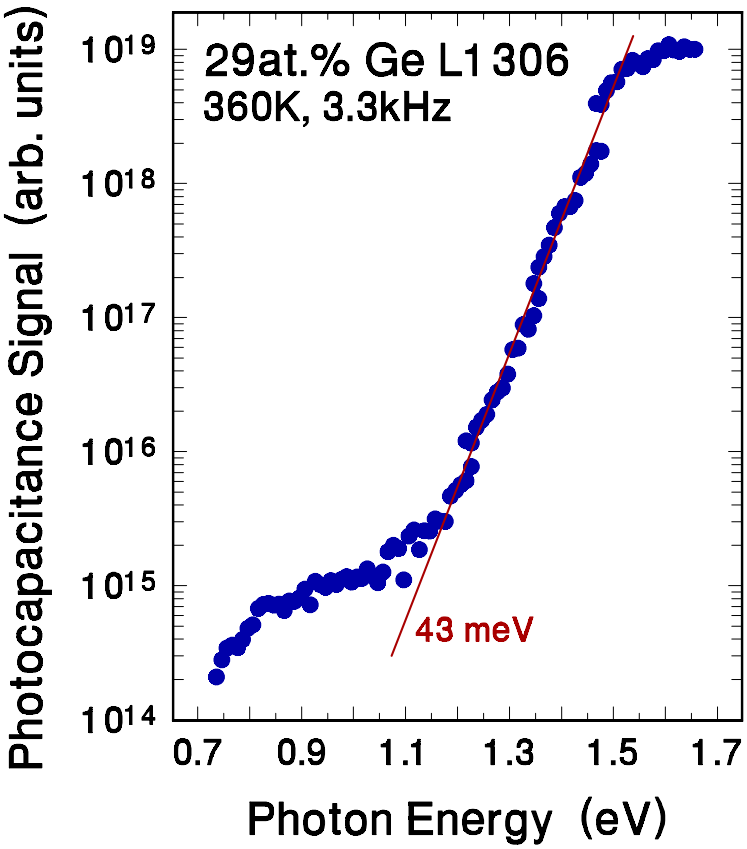

FIG. 5. Transient photocapacitance spectrum for the 29at.% Ge alloy sample. The Urbach energy deduced for this sample, indicated by the thin line, is roughly 43meV. This is as low as even the best pure a-Si:H films measured by the TPC technique. The deep defect band exhibited below 1.0eV has a magnitude that indicates a deep defect density in the mid 10^{15} cm^{-3} range.

However, an even clearer indication of the improved quality of this HWCVD a-Si,Ge:H sample is apparent in the TPC spectrum displayed in Fig. 5. Our previously best characterized set of NREL HWCVD alloy samples had indicated that, as the Ge fraction was increased from 5at.% to 20at.%, the Urbach energy increased from 45meV to 55meV.[1] The magnitude of the deep defect band in those previous samples increased more than five-fold to more than 10^{16} cm^{-3} for 20at.% Ge. In contrast, the data in Fig. 5 indicate an Urbach energy of only 43meV for this 29at.% film, and a deep defect band in the mid 10^{15} cm^{-3} regime.

The spectrum in Fig. 5 clearly demonstrates that high quality a-Si,Ge:H can be obtained using the hot-wire CVD growth process. This dispels the notion that energetic ion bombardment is somehow important for the production of the best a-Si,Ge:H alloys since, in the HWCVD process, no such ions are present. It is also noteworthy that these samples were deposited at growth rates significantly higher than the best PECVD alloy samples. Further studies on this series of samples will of course be necessary to fully evaluate their electronic properties. Plans for the near future include comparisons of transient photocapacitance with transient photocurrent spectra to get some idea about the efficiency of hole collection. Light-induced degradation studies will also be started shortly, and a greater range of alloy compositions need to be examined before we can formulate any authoritative conclusions regarding the real success of this low temperature hot-wire process.

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1. J.D. Cohen, NREL Technical Report SR-520-32525 (2002), p. 55.